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CORROSION PERFORMANCE OF METALS AND ALLOYS IN A TUFF GEOCHEMICAL ENVIRONMENT

R. A. Van Konynenburg
and
R. D. McCright

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R. A. Van Konynenburg and R. D. McCright
Lawrence Livermore National Laboratory
Livermore, CA 94550

ABSTRACT

Reference and alternate alloy systems have been chosen for use in fabricating waste packages for a potential high-level nuclear waste repository in tuff. The main corrosion concerns have been identified. Testing performed to date indicates that austenitic stainless steels would perform well as package materials under the expected conditions as well as the less likely extreme conditions so far postulated. Carbon steel appears to be adequate as a material for borehole liners. Copper-based alloys and Zircaloys are also undergoing corrosion testing, the former as alternate package materials, and the latter because of their presence as spent fuel cladding.

INTRODUCTION

The Nuclear Regulatory Commission has established a requirement[1] that packages for high-level nuclear waste provide containment that is "substantially complete" for a period of between 300 and 1,000 years after permanent closure of a repository. One of the major considerations in designing packages to meet this requirement is corrosion in the particular geochemical environment expected to be present in the repository.

On December 19, 1984, the Department of Energy identified three sites as being the leading candidates for location of the first U.S. high-level nuclear waste repository, one of which is located in tuff rock at Yucca Mountain in Nevada. Lawrence Livermore National Laboratory is responsible for waste package development for this site, as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. This paper briefly describes the reference designs, reviews the criteria for selection of metals and alloys to be used in fabricating high-level waste packages, and discusses the expected environmental characteristics of a tuff repository that are important to corrosion. The main candidate materials are listed, as are the chief corrosion mechanisms that are expected to be of concern. Recent progress in corrosion research and testing for the tuff repository is described, and the current status of corrosion performance data is reported.

REFERENCE WASTE PACKAGE DESIGNS

Reference package designs[2] have been developed for three high-level waste forms: spent fuel, West Valley commercial high-level waste glass, and defense high level waste glass. The West Valley glass is expected to be similar to the defense glass. These designs feature a welded container having a 1-cm wall thickness for the spent fuel, and welded containers (overpacks) of similar thickness that will enclose the glass pour canisters.

CRITERIA FOR SELECTION OF METALS AND ALLOYS

In choosing materials for tuff repository waste packages, four main criteria are important: corrosion behavior, mechanical properties, fabricability, and cost. Of these criteria, the corrosion behavior receives the greatest attention because of the long-term containment requirements.

The corrosion must not only occur at a sufficiently low rate so that a reasonable thickness of material will suffice. It must also be as predictable as possible in terms of mechanisms and rates so that there can be sufficient confidence in predictions of long-term corrosion behavior.

The materials chosen must have sufficient strength at the operating temperatures to withstand the stresses during lifting and handling. Ductility is important not only in fabrication, but also in handling. A reasonable amount of fracture toughness is desirable to provide safety in case of accidentally dropping a package. Further, the ductility and fracture toughness properties must be retained at high levels for at least 50 years after repository closure to meet the NRC retrievability requirements.

Fabricability refers to the ease of working the metal or alloy to the desired shape and thickness. It is closely related to the ductility and toughness of the material. Waste containers could be fabricated by a number of different methods, some of which would entail the use of assembly welds to join the components together. After the containers are filled, they will be sealed by a welding process that could either be autogenous or could make use of a filler material.

The fabrication and sealing processes may give rise to microstructures and residual stresses that could adversely affect the corrosion behavior and hence, the long-term containment performance. For this reason, the process specification for producing the containers must be developed with the containment requirement in mind.

Finally, it is important that the cost be both reasonable and as low as possible, consistent with a high degree of reliability in meeting the containment requirement. Implicit in the cost criterion is the requirement that a sufficient amount of the selected material must be available during the time period when it will be needed.

ENVIRONMENTAL PARAMETERS IMPORTANT TO CORROSION

The prediction of corrosion behavior over the time periods of interest for this application is generally recognized to be a very challenging problem, since corrosion experiments and tests will necessarily be limited to a maximum of a few years in duration. Predictions must therefore be based on theoretical models of corrosion behavior that are anchored as solidly as possible to data from experiments and tests that explore a wide range of mechanisms, for times as long as are practicable. In carrying out studies of this sort, one can gain a great deal of insight from the body of knowledge already accumulated in corrosion science and engineering. Past experience shows that certain features of a repository environment could have important effects on corrosion processes in general. These include the physical state of the corrosion medium (liquid or gaseous), the chemical makeup of the medium, the temperature, the pressure, the pH, the redox potential, the flow rate, and the presence of ionizing radiation. Efforts are being made to determine the ranges of values that could occur for these parameters at the proposed tuff repository site, to reproduce these conditions in the laboratory, and to determine the sensitivity of the corrosion behavior of the candidate materials to these environmental parameters.

EXPECTED CORROSION ENVIRONMENT IN A REPOSITORY IN TUFF

The proposed location for a repository in tuff is in the Topopah Spring member of the Paintbrush tuff under Yucca Mountain, on federal land 100 miles northwest of Las Vegas, Nevada.

Although more detailed characterization of this site remains to be performed, the essential features have been elucidated on the basis of available data.[3] In projecting the corrosion environment, we must take account not only of the natural state of the site, but also of changes introduced by the presence of the repository and the waste packages.

One of the key features of the tuff site is that the repository is to be located at a horizon that is well above the water table. Because of this and the fact that the rock is not expected to creep significantly under the lithostatic load, the pressure in the repository is expected to remain near atmospheric for the selected elevation. As a result, so long as the temperature is above the local boiling point of about 95°C., the corrosion medium at the package surfaces will be totally gaseous, composed of steam and air. For the higher heat output waste forms, such as spent fuel, this gaseous period could last for as long as 1,000 years or more.[2] For cooler waste forms, such as defense high-level waste, liquid water would begin condensing on the packages much earlier, perhaps at 200 years.[2] Even after water could condense, it is considered highly unlikely that the packages would ever become inundated, because of the low influx of water (less than 1 mm per year infiltration at depth from rainfall), the permeable nature of the rock, and the favorable drainage conditions of the particular geologic setting.

The rock itself is classified as densely-welded, devitrified tuff. It consists of a fine-grained matrix surrounding larger phenocrysts. The major mineral species present are quartz, cristobalite, and alkali and plagioclase feldspars. An approximate chemical composition of the whole rock is given in TABLE I.[4] (The iron is present mostly in the ferric state.)

The composition of the infiltrating water is believed to be well represented by that obtained from well J-13, which is located near the proposed repository site and penetrates the Topopah Spring tuff. The composition of J-13 well water is shown in TABLE II.[5] This is seen to be a bicarbonate groundwater, with relatively small concentrations of halide ions.

TABLE I

Approximate Chemical Composition of Topopah Spring Tuff[4] (Whole Rock) (Wt. %)

SiO_2	75.2
Al_2O_3	12.4
K_2O	4.8
Na_2O	3.1
Fe_2O_3	1.8
CaO	0.5
MgO	0.2
TiO_2	0.1
MnO	0.06
Loss on ignition	1.0
Total	99.16

TABLE II

Dissolved Species in J-13 Well Water[5] (mg/L)

HCO_3	130
SO_4	18
NO_3	9
Cl	7
F	2
Na	43
Ca	13
K	6
Mg	2
Si	27

Temperatures of the package surfaces will depend on design details but are expected to range up to about 270°C.[2] The pH is expected to remain near neutral or slightly alkaline for water in contact with the rock.[5] In regions of the package surfaces not in contact or in liquid diffusive communication with the rock, it is possible that lower pH values could arise, because of radiolytic formation of nitric acid in the gas phase,[6] followed by condensation onto the surfaces. In these regions, the acid would not be buffered by exchange of H^+ with anions from the feldspars in the rock.

The redox condition in the tuff repository will be oxidizing because of the presence of air, the absence of a significant concentration of reducing species (such as ferrous iron) in the rock, and the presence of ionizing radiation. Since the reference package designs have relatively thin walls (about 1 cm), the gamma dose rates may range as high as 1 kGy per hour (10^5 rads per hour).

METALS AND ALLOYS UNDER CONSIDERATION

The reference alloy system chosen for tuff repository waste package designs is the austenitic stainless steels. This choice was made using the criteria mentioned above, noting particularly the oxidizing nature of the environment and the relative lack of halides. The fact that 304L stainless steel has been chosen as the reference material for Savannah River defense high-level waste glass pour canisters[7] makes our reference material particularly compatible for the DHLW case. Further, documented experience under conditions similar to those in tuff was obtained from the Climax test, in which spent fuel in 304L stainless steel canisters was stored in a granite facility for three years to demonstrate the technical feasibility of geological storage. Finally, the existence of a range of alloys in this class (e.g., 304L, 316L, 321, and Incoloy 825) provides the flexibility to make a specific choice to combat particular forms of corrosion found to be important.

The alternative alloy system for packages in tuff is copper-based, including CDA 102 oxygen-free high-conductivity copper, CDA 613 aluminum bronze, and CDA 715 70/30 cupronickel. This choice provides a completely different class of materials, giving protection against the possible but, we believe, unlikely discovery of a "fatal weakness" of austenitic stainless steels in this application.

In addition to these package materials, we are testing low-carbon steel as a possible material for borehole liners, should these be found necessary to provide stability for the required retrievability period. The corrosion behavior of Zircaloy-2 and -4 is also being examined, since they will be present as spent fuel cladding, and may serve as important barriers to radionuclide migration.

MAIN CORROSION CONCERNS

There are many known corrosion mechanisms, and package developers must be alert to all of them, as well as to interactions between them and the unlikely, but possible, appearance of mechanisms heretofore unknown. A starting point can be found in past experience, which indicates that the particular mechanisms that are dominant depend on the metal or alloy used, its thermomechanical condition, and the thermal and chemical environment.

In the case of austenitic stainless steels in the type of environment described, general corrosion is not expected to be the limiting mechanism. Rather, the main concerns are localized and stress-assisted forms of corrosion. Although the composition of J-13 water appears to be relatively benign, we must be alert to the possibility that the dissolved species could become more concentrated by the distillation of vadose water dripping onto hot containers, for example. More concentrated electrolytes could possibly give rise to pitting, crevice corrosion, or transgranular stress corrosion cracking.

Sensitization, which consists of the depletion of chromium from grain boundaries as a result of the formation of chromium carbide, could result either from the relatively brief high-temperature processes of glass pouring and welding or from the relatively long "soak" at lower temperatures in the repository. This sensitization could make the material vulnerable to intergranular stress corrosion cracking as well as other forms of localized corrosion.

The copper-based materials would likely be subject to general corrosion as well as to localized and stress-assisted corrosion mechanisms. The formation of nitric acid by irradiation of moist air could be particularly significant for copper alloys.

Low-carbon steels would be expected to be subject to the same mechanisms as would copper-based materials. In addition, one would need to consider hydrogen embrittlement, which could result from the hydrogen released either by corrosion or radiolysis.

The Zircaloys are expected to be quite resistant to corrosion in the tuff environment, particularly since they will not be exposed to large amounts of air and water vapor until after the waste package has been breached, and temperatures are low. Nevertheless, we must pay particular attention to the possibilities of stress corrosion cracking and hydrogen embrittlement.

REVIEW OF CORROSION RESEARCH AND TESTING FOR THE TUFF REPOSITORY

Our strategy is threefold: first, we test the materials of interest under the conditions expected in the tuff repository for durations as long as are practicable. If their performance is satisfactory, we then test under more extreme and less likely conditions, both to provide assurance against uncertainty in our assessment of the environment and to find out the limiting conditions for satisfactory performance of the materials. Finally, we perform research to develop an understanding of the basic mechanisms of corrosion to enable us to develop models that can be used to project future behavior with some confidence.

Most of our corrosion work up to this time has been concerned with austenitic stainless steels and carbon steels. A small amount of work has also been performed on copper-based materials and Zircaloys. The stainless steel tests have involved weight change measurements on coupons with crevices to evaluate general corrosion rates and crevice corrosion in steam and liquid water with and without irradiation. To study stress corrosion, we have performed U-bend tests with and without irradiation, slow strain rate tests, and bent beam stress corrosion tests. We have made efforts to intentionally sensitize some specimens, and we have performed some tests in water with concentrated solutes. Electrochemical measurements in aqueous media have been conducted with and without a radiation field. Results of this work have been and are being reported elsewhere.[8,9]

As expected, we have found that general corrosion of austenitic stainless steel, in particular Type 304L, is not a significant problem in the expected environment. A conservative estimate of the wastage over 1,000 years has been placed at 1 mm.[8] No evidence of pitting or crevice corrosion on 304L has thus far been seen, after exposure times of up to 10,000 hours in boiling J-13 water.

Efforts to sensitize 304L stainless steel by cold-working, welding, and heat treating at 600°C for as long as 24 hours have so far not succeeded in inducing stress corrosion cracking, after 12 months of exposure in irradiated J-13 water. Electrochemical tests have confirmed the unlikelihood of pitting and crevice corrosion in irradiated and unirradiated environments. In summary, all tests performed so far indicate that 304L stainless steel would perform well under the expected conditions as well as in less likely extreme cases of severe sensitizing treatments, greatly concentrated electrolytes, gamma dose rates up to 6 times the expected maximum, and complete inundation.

An analysis[10] was performed to predict whether 304L stainless steel would undergo a "low temperature" sensitization process during the lengthy period (centuries) at moderately elevated temperatures (100-270°C) after emplacement of the waste package containers in the repository. Extrapolation of the time-temperature-sensitization data for heavily cold worked 304L with a carbon content (0.028%) at the high end of the permitted range indicated that this steel would sensitize in 10 years at 280°C. Since these conditions approach a situation that some containers could experience, certain degrees of conservatism will be employed to minimize sensitization. Reduction of the peak temperature and the duration at the peak temperature are important means of retarding sensitization. Adjustment of the power loading and configuration of the spent fuel assemblies in waste package design can reduce the container temperature. Other approaches are use of 316L rather than 304L, or use of the LN grades of stainless steel. The additional alloying elements in these materials hinder diffusion of carbon, which is a precursor to chromium carbide formation and sensitization. Further, process control to reduce the amount of residual stress from fabrication and welding alleviates the sensitization problem. These approaches were identified and discussed elsewhere.[11] Future testing will involve more extensively 316L and 316LN and special modification of these materials. In addition to greater resistance to sensitization, these materials are expected to show greater resistance to pitting and crevice corrosion should concentration of ionic species in the water occur.

The work on carbon steels[12] has included (1) a weight loss test to determine the general and localized corrosion rates of carbon steel and other Fe-based materials in J-13 water at various temperatures, (2) an electrochemical polarization test to determine the corrosion potentials and currents as a function of temperature, (3) a general and localized corrosion test of unstressed specimens exposed to J-13 water and to saturated steam at 100°C., (4) a bent beam stress corrosion susceptibility test of welded specimens in 90°C J-13 water, and (5) corrosion tests of specimens exposed to irradiated J-13 water.

The results indicate that carbon steel does not suffer excessive corrosion in these environments. It also appears to be resistant to stress corrosion cracking in the modes tested. The localized corrosion was usually found to be 1-3 times as rapid as the general corrosion. The crevice corrosion rate in wet steam was as much as 15 times the general rate. Projections from the available data indicate that carbon steel would have a service life longer than 50 years after repository closure providing the repository is not inundated, and thus that carbon steel would be a satisfactory material for borehole liners.

Preliminary results from crevice corrosion tests of copper-based materials in room-temperature irradiated moist air indicate some susceptibility to attack under these conditions. This was expected from previous work.[13-15] More extensive testing is underway to quantify these results.

Preliminary corrosion tests of irradiated Zircaloy cladding have not shown any clearly observable corrosion so far.[16] Testing is continuing.

Since significant gamma ray dose rates will be present for some waste forms in the tuff repository, and since radiation effects on corrosion mechanisms are not well understood, we have initiated experiments directed toward developing such an understanding.[17] We have performed electrochemical measurements using samples of austenitic stainless steels, platinum, and copper-based materials in J-13 water and more concentrated solutions with and without gamma irradiation. With 316L stainless steel, the corrosion potential was found to shift in the positive direction by about 150-200mV when a gamma field of about 3 Megarad per hour was applied. This shift has been attributed to the production of .OH and H_2O_2 in the solution. It was also found that the pitting potential was shifted by about the same amount, indicating that gamma irradiation should not increase the susceptibility of 316L stainless steel to pitting in these solutions.

CURRENT STATUS

All testing to date suggests that austenitic stainless steels will perform well as waste package materials in the environments expected in the tuff repository. Likewise, carbon steel shows every indication of being an adequate material for use in borehole liners. The Zircaloys show considerable promise for providing "defense in depth" against radionuclide migration from spent fuel. More extensive testing is underway to quantify the behavior of the copper-based materials.

Future work on the austenitic stainless steels will include longer stress corrosion tests in order to detect possible low-temperature, long-time sensitization and deleterious microstructural changes such as development of sigma phase regions. Efforts will be made to intentionally sensitize the material in order to find out what extreme conditions are necessary to do so. Electrochemical measurements will explore the effects of elevated temperature and concentrating the ionic species in J-13 water.

Testing to date has focussed on the initiation of localized and stress corrosion. Future work will be aimed at measuring the environmental and material effects on the propagation of these attack modes by testing pre-pitted and pre-cracked specimens. Also, general, localized, and stress corrosion tests will be conducted on specimens with applied electrochemical potentials of appropriate magnitudes to simulate irradiated environments and will permit us to enlarge the presently limited data base on corrosion performance of materials under irradiation.

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